

First-Principles Investigation of Hydrogen Interaction with Functionalized Carbon Nanomaterials

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ABSTRACT

Although hydrogen is considered a key component of the future clean-energy economy, the utilization of hydrogen as an on-board fuel is hindered by lack of a fuel storage medium with high gravimetric capacity, high volumetric capacity, moderate operating pressure and temperature and fast, reversible sorption kinetics. Carbon nanomaterials, such as graphene, carbon nanotubes (CNTs) and fullerenes, have been the focus of continuous research as storage scaffolds due to their extremely high specific surface area, chemical tunability and low mass density. Pure carbon surfaces, however, interact with molecular hydrogen via weak van der Waals forces that give it an adsorption energy that is too small to allow it to be reversibly stored at room temperatures. The methodological principles of DFT-based studies of hydrogen adsorption are presented, and the importance of accounting for dispersion interactions in physisorption dominated systems is emphasized. Representative results are compared in the doped graphene, decorated nanotubes and metal-functionalized fullerenes and the bonding mechanisms (physisorption, Kubas-type orbital interaction, spillover and ionic binding) are discussed. The problems such as metal-cluster agglomeration, the error in the standard exchange-correlation functionals for van der Waals dominated systems, and the mismatch between the capacities calculated by the computer and experimentally measured are critically studied. Finally, the review summarizes some directions for future first-principles research, such as machine-learning-assisted screening and the creation of multiscale frameworks that link predictions of electronic structure to device performance.

Keywords: *Density Functional Theory; Hydrogen Storage; Functionalized Graphene; Carbon Nanotubes; Metal Decoration; Kubas Interaction; Van Der Waals Correction; First-Principles Simulation.*

INTRODUCTION

Global interest in hydrogen as an energy carrier has increased as a result of the shift away from energy based on fossil fuels. The gravimetric energy density of hydrogen is very high (about 120 MJ/kg, which is about three times that of gasoline) and if it is produced using renewable electricity through electrolysis it is a route to a truly carbon neutral fuel cycle. Hydrogen has, however, not yet been widely used in mobile and stationary applications, due to the technical challenge of storing it safely, compactly and reversibly (Faye, O., Eduok, 2017). Current storage methods are energy intensive, requiring high-pressure compression (35-70 MPa), or cryogenic liquefaction (20 K) and are therefore very costly in terms of engineering and safety requirements. Solid-state storage, where hydrogen is bound to or embedded in a host material, has thus proven to be an attractive alternative, and decades of materials-discovery have been dedicated to metal hydrides, complex hydrides, metal-organic frameworks and carbon-based nanomaterials. Carbon nanomaterials have a special place in this scenario (Mollaamin, F., & Monajjemi, M. 2024).

In addition to having very high specific surface areas (in theory approaching 2630 m²/g for a single sheet of graphene), graphene, single and multi-walled carbon nanotubes and fullerenes have a low atomic mass, chemical robustness, and in the case of carbon nanotubes and fullerenes, well-defined pore or cage geometry which can be used for confinement effects (Faye, O., Szpunar, J. A., Szpunar, B., & Beye, A. C. 2017). Initial hopes for these materials to meet the near-term on-board hydrogen storage gravimetric targets of the United States Department of Energy (DOE) were tempered by the realization that pure sp² carbon surfaces interact with molecular hydrogen almost entirely through non-directional, weak

van der Waals forces. The resulting physisorption energies, which are generally in the range 0.02-0.06 eV per H₂ molecule, are too small to allow for large hydrogen storage at ambient temperature, and significant hydrogen uptake is only achieved at low temperatures, bringing back many of the practical challenges that were supposed to be overcome by solid-state storage (Mananaghaya, M., Yu, D., Santos, G. N., & Rodulfo, 2016).

This restriction has stimulated a vast research effort in the functionalization of carbon nanomaterials, which refers to the systematic alteration of the carbon lattice by substituting the atoms by heteroatoms (doping), chemically attaching chemical moieties, or decorating the carbon lattice with metal atoms or clusters with the specific goal of making the hydrogen binding energy range from 0.2-0.6 eV per H₂ molecule, which is thermodynamically favorable for reversible storage under moderate conditions (Verdinelli, V., Juan, A., & German, 2019). First principles quantum mechanical methods and specifically density functional theory (DFT) is now the main method to explore this design space. DFT provides the ability to compute the electronic structure of a proposed material that is functionalized, without the need to make use of any empirically fitted interatomic potentials, and can predict the adsorption energies, charge-transfer characteristics and structural stability of candidate materials before they can be synthesized experimentally (Gangan, A., Chakraborty, 2019).

BACKGROUND

Thermodynamic requirements for reversible hydrogen storage

The enthalpy of hydrogen adsorption is the main factor that determines the suitability of a candidate storage material. When the binding energy is low (0.02-0.06 eV per H₂ molecule as is the case for pristine carbon, physisorbed), the amount of hydrogen which can be retained at cryogenic temperature is limited, and otherwise the hydrogen can be desorbed easily at 298 K. For many covalent metal hydrides the binding energy is too high, typically greater than 1 eV per hydrogen atom, making the release of hydrogen unfeasibly high temperatures for practical purposes and hence compromising the reversibility of the storage cycle and its energy efficiency. It has been widely reported that a target reversible window is between about 0.2-0.6 eV per H₂ molecule (desorption temperatures in the range of 70–300 K that are relatively compatible with proton exchange-membrane fuel cells. Intermediate strength binding regime is the most challenging regime to be obtained with unmodified sp² carbon and is the main design goal of the functionalisation approaches discussed in Section 4 (Anikina, E., Banerjee, 2019).

Structural forms of carbon nanomaterials relevant to hydrogen storage

Graphene is an atomically thin layer of sp²-hybridized carbon in a honeycomb lattice, which is the highest theoretical specific surface area of any carbon allotrope, and is the prototype 2D substrate for studies of functionalization. Single-walled carbon nanotubes (SWCNTs) are created by rolling a graphene sheet into a seamless cylinder, inducing rehybridization of the carbon p_z orbitals, which results in slightly higher reactivity of the tube wall than in flat graphene, and a tube interior pore that can accommodate the confinement-enhanced physisorption (Muhammad, R., Shuai, Y., 2017). Other types of carbon nanotubes such as multi-walled carbon nanotubes and bundled SWCNT arrays also contain interstitial and inter-tube channels which have been suggested as secondary adsorption sites. The fullerenes (closed-cage carbon molecules) are finite molecules with a much curved surface, whose outside and inside can in principle be made functional and which have a molecular rather than extended character, giving them the advantage of being comparatively easy to benchmark with first-principles models of very high accuracy (Yadav, S., Tam, J., & Singh, 2015).

Functionalization strategies

The first principles literature is full of three general approaches to functionalization. When atoms other than carbon are introduced into the lattice, they are called heteroatom doping, which causes the local electronic structure to be changed, and polarization regions of enhanced charge density or electron deficiency are created that can polarize approaching hydrogen molecules. Surface functionalization can be accomplished via covalent bonding of functional groups at the surface, typically hydroxyl (-OH) and carboxyl (-COOH) groups, which can alter the electrostatic environment and also introduce hydrogen-bonding pathways. Metal decoration, where alkali (Li, Na), alkaline-earth, or transition-metal (Ti, Sc, Pd, Pt) atoms are adsorbed onto the C surface, is typically most successful to significantly increase the hydrogen binding energy through the addition of strong ionic/electrostatic fields (alkali metals) or partially filled d-orbitals that can interact with the H-H sigma bond (transition metals). In mechanistic detail such mechanisms are discussed in Section 4 (Banerjee, P., Thapa, R., Rajkamal, A., Chandrakumar, K. R. S., & Das, 2019).

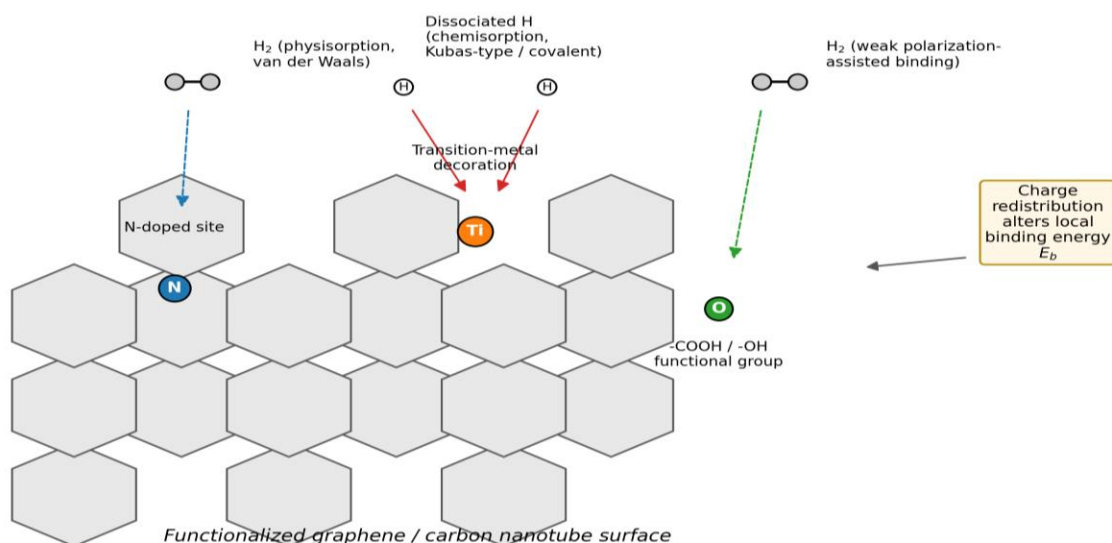


Figure 1: Schematic representation of hydrogen interaction mechanisms on functionalized carbon nanomaterials, illustrating van der Waals physisorption, polarization-assisted binding at oxygen-functionalized sites, and Kubas-type/dissociative chemisorption at transition-metal-decorated sites

FIRST-PRINCIPLES COMPUTATIONAL METHODOLOGY

Density functional theory framework

The vast majority of first-principles studies of hydrogen adsorption on carbon nanomaterials are carried out in the framework of the Kohn-Sham approximation to density functional theory (DFT), in which the many-body electronic Schrodinger equation is replaced by a collection of density-functional single-particle equations, which are coupled by the electron density. The exchange and correlation effects are not exactly calculable and are approximated using an exchange-correlation functional, the generalised gradient approximation (GGA) has been widely used in this literature due to its good accuracy and its relatively low computational cost for periodic slab and nanotube models. For periodic graphene and nanotube supercell calculations, the plane-wave basis sets with projector-augmented-wave (PAW) or ultrasoft pseudopotentials (USP) are generally used, such as in codes like VASP and Quantum ESPRESSO, whereas for larger functionalized systems, where plane-wave calculations are impractical, localized-basis codes, like SIESTA, are commonly employed (Yu, H., Luo, H., Cai, J., & Dong, 2019).

Dispersion corrections

One methodological aspect of special relevance is the lack of standard GGA functionals to describe long-range van der Waals dispersion forces, which are the major forces in the physisorption of H₂ on pristine and weakly functionalized carbon surfaces. The physisorption well that is observed in experiments can thus be significantly under-estimated and sometimes even mis-predicted by uncorrected GGA calculations. Most commonly, the Grimme DFT-D2 and DFT-D3 schemes are used to compute the atom-pairwise attractive contribution to the GGA total energy, which has come to be essentially standard practice in this literature. More first-principles treatment of dispersion is achieved with non-local van der Waals density functionals, such as vdW-DF and its upgrades (vdW-DF2). They are often used as a benchmark for testing against the D2/D3-corrected GGA results. For the most strenuous benchmark calculations, the quantum Monte Carlo or random-phase-approximation (RPA) methods have been used on small model systems to obtain benchmark binding energies for comparison with cheaper approaches.

Adsorption energy and structural analysis

The hydrogen binding (or adsorption) energy is often defined as $E_b = E(\text{substrate}+n\text{H}_2) - E(\text{substrate}) - nE(\text{H}_2)$, where $E(\text{substrate}+n\text{H}_2)$ is the total energy of the functionalized carbon system with n hydrogen molecules adsorbed, $E(\text{substrate})$ is the total energy of the bare functionalized system, and $E(\text{H}_2)$ is the total energy of an isolated hydrogen molecule in the same simulation cell (Sharma, V., Kagdada, 2020). The negative E_b value means that the adsorption process is thermodynamically favored (exothermic), with the value of E_b compared to the targeted window mentioned in Section 2.1. Typical analyses that are performed in parallel with the binding energy are the Bader or Mulliken charge-transfer analysis (to characterize ionic or covalent nature of the metal-hydrogen or dopant-hydrogen interaction), the electron density

difference plot (to visualize charge redistribution upon adsorption), the phonon or ab initio molecular dynamics calculation (to assess the thermal and kinetic stability of the functionalized structure, and in particular whether decorating the metal atoms leads to clustering), and the projected density of states (PDOS) in periodic graphene/nanotube studies to reveal hybridization between the dopant/metal orbitals and the H₂ molecular orbitals responsible for the activation of the bond.

Summary of representative methodological choices

Table 1 shows that despite methodological consistency, there are also areas of ongoing methodological debate, especially when it comes to the use of dispersion correction, that characterize this field, as reflected in the exchange-correlation functionals, basis sets/codes and dispersion-correction schemes used in a representative subset of the studies reviewed in Section 4.

Table 1: Representative computational methodologies employed in first-principles studies of hydrogen adsorption on functionalized carbon nanomaterials

Study focus	Exchange-correlation functional	Basis set / code	Dispersion correction
Pristine & N-doped graphene	GGA-PBE	Plane-wave (VASP, PAW)	DFT-D2 (Grimme)
Li/Ti/Sc-decorated graphene	GGA-PBE, hybrid B3LYP (validation)	Plane-wave (Quantum ESPRESSO)	DFT-D3 (Grimme, BJ damping)
Carboxyl/hydroxyl-functionalized CNTs	GGA-PBE	Gaussian basis (SIESTA)	DFT-D2
Pd/Pt-decorated CNTs and fullerenes	GGA-PBE, PBE0 (benchmarking)	Plane-wave (VASP)	DFT-D3
B/N co-doped porous carbon	GGA-PBE	Plane-wave (CASTEP)	TS scheme
Benchmark H ₂ physisorption energetics	vdW-DF2, RPA (reference)	Plane-wave (VASP)	Non-local vdW functional

HYDROGEN INTERACTION MECHANISMS ACROSS FUNCTIONALIZATION STRATEGIES

Heteroatom-doped graphene and nanotubes

The use of N or B as substitutional lattice dopants, which are well studied via first-principles calculations, is partly because the method is well known synthetically and partly because it results in relatively weak and clean perturbations of the pristine physisorption picture. The doping significantly modifies the interaction between the approaching H₂ molecule and the nitrogen site by placing a locally electron-rich site near the approaching molecule (which could be pyridinic or graphitic nitrogen configurations, both of which are commonly modeled), leading to weak polarization of the approaching molecule and a shallow charge transfer contribution to the van der Waals-dominated interaction (Valencia, H., Gil, A., & Frapper, 2015). Nearly all reported binding energies for H₂ at nitrogen doped sites in graphene in the literature fall in the 0.07-0.12 eV per H₂ range, which is still double that of pristine graphene, but is still within the desired window for ambient-temperature reversible storage. The electron deficient nature of the boron site gives rise to a qualitatively similar, although slightly greater improvement, upon boron doping, due to a different, but likewise weak polarization interaction with the H₂ sigma bond. However, a further, but more marginal, improvement in binding energy has been reported when co-doping with both nitrogen and boron (usually at neighbouring lattice sites to form a locally polarized B-N pair), which is thought to be a result of the dual electron-donating and electron-withdrawing properties.

One clear conclusion from this work is that heteroatom doping alone increases the H₂ binding energy by about two to three times when compared to pure carbon, but it does not appear to attain the thermodynamically desirable range. In spite of this, doped sites are still of practical importance since in many of the studies described in Section 4.3, it has been found that the presence of a nearby dopant atom can actually reduce the tendency to decorate the metal atoms to migrate and agglomerate a failure mode which is discussed in further detail in Section 5.1.

Covalent oxygen-functionalization

Another easily accessible site for covalently attaching functional groups to graphene and nanotube surfaces that has been studied computationally is the hydroxyl and carboxyl groups, which can be readily produced experimentally through an oxidative treatment, such as that used to create graphene oxide. First-principles calculations show that the functional group containing oxygen creates a local dipole, and for carboxyl groups, a donor/acceptor site for the H₂ molecule that can interact with the molecule via a combination of electrostatic and weak hydrogen-bonding interactions. The binding energies

for H₂ at near –COOH functionalised carbon sites are normally in the range of 0.10-0.16 eV per H₂ although improved over pristine and doped carbon, this is still too low within the target window (Luna, C. R., Verdinelli, V., German, 2015). Another issue highlighted in this literature is that heavy oxygen functionalization can break the sp² conjugation of the underlying carbon lattice, which may lead to decreased electrical conductivity and mechanical strength, and therefore, may be undesirable in integrated storage and conduction applications like hybrid super capacitor-storage devices. The discussion of oxygen functionalization is therefore more often in the context of complementing oxygen-free approaches to achieve the desired storage capacities for oxygen-related DOE activities, such as dispersion and processing of oxygen-free carbon nanomaterials or subsequent decoration of these with metals (Mondal, B., & Chakraborty, 2024).

Metal decoration and the Kubas mechanism

The strategy most often found in the first-principles literature reviewed here to be used in functionalizing carbon nanomaterials for hydrogen storage is to decorate with metal atoms for which the binding energies are within, or near to, the thermodynamically favorable range for reversible hydrogen storage. There are usually two sub-classes which are distinguished in a completely different manner. Alkali-metal decoration (most commonly lithium) takes place in a predominantly ionic mode: the alkali atom loses its valence electron to the carbon substrate, it is now a positively-charged adatom, and the electric field of the adatom is able to polarise and weakly bind a number of neighbouring H₂ molecules via an ion-induced-dipole interaction. This mechanism can accommodate a number of H₂ molecules per metal center, as has been reported in several DFT studies of lithium-decorated graphene, and has been shown to have gravimetric capacities of > 5 wt% (although the binding energies are on the low end of the desired range, ~ 0.15-0.20 eV per H₂ molecule).

The interaction between the transition metals and the decoration is a different type, and usually stronger, than in the case of the lanthanides, as it is found that transition metals (specifically, those of the early transition metals such as titanium, scandium and vanadium) tend to interact with decoration in a different way; the Kubas model developed in organometallic chemistry for complexes of molecular hydrogen is often used to describe this interaction (Jha, S. K., Roth, M., Todde, 2018). In this mechanism, the partially filled d-orbitals of the decorating metal atom donate electron density to the antibonding sigma orbital of the H₂ molecule, while accepting electron density from the H₂ bonding sigma orbital, thus weakening the H-H bond (or even breaking it at high binding strength) and forming a relatively strong metal-H₂ interaction.

DFT calculations of the binding energies of H₂ on decorated graphene surfaces are generally found to be in the desired range (0.35-0.45 eV per H₂ molecule) and several calculations also suggest that a single adatom of Ti may bind three to four molecules of H₂, corresponding to gravimetric capacities of 6 wt% or higher, based on the decorated-cluster model. Hydrogen binding energies achieved by palladium and platinum decoration are reported to be even stronger, in some cases with complete dissociative chemisorption to atomic hydrogen (binding energies greater than 0.5 eV per H atom) that can begin to approach the upper limit of, and in some cases surpass the reversibility window and may complicate low-temperature desorption.

Synthesis of comparative trends

The binding energies and gravimetric capacities presented in Table 2 and the graph in Figure 2 are summarizing the results reported in representative studies from the literature cited in this section, but they do not represent all the available data in the literature. There are two trends: First, the binding energy systematically increases in the order pristine < heteroatom-doped < oxygen-functionalized < alkali-metal-decorated < transition-metal-decorated, reflecting the increasingly strong and directionally controlled nature of the interaction that drives their binding. First, the binding energy follows the trend pristine < heteroatom-doped < oxygen-functionalized < alkali-metal-decorated < transition-metal-decorated, in accordance with the increase in the strength and directionality of the underlying interaction mechanism (Choudhary, A., Malakkal, L., Siripurapu, R. K., Szpunar, B., & Szpunar, 2016).

Second, gravimetric capacity is not monotonically related to binding energy: high capacity at relatively low binding energy is possible for the alkali metals in that they can coordinate multiple H₂ molecules, while the strongest transition-metal binders may not be the best in terms of number of H₂ molecules coordinated per metal center because bonds between the metal center and H₂ molecules are too strong to allow the binding of multiple molecules at the same center without steric or electronic effects. This separation between binding strength and capacity can be significant and, like other binding-energy data, is not easily discernible.

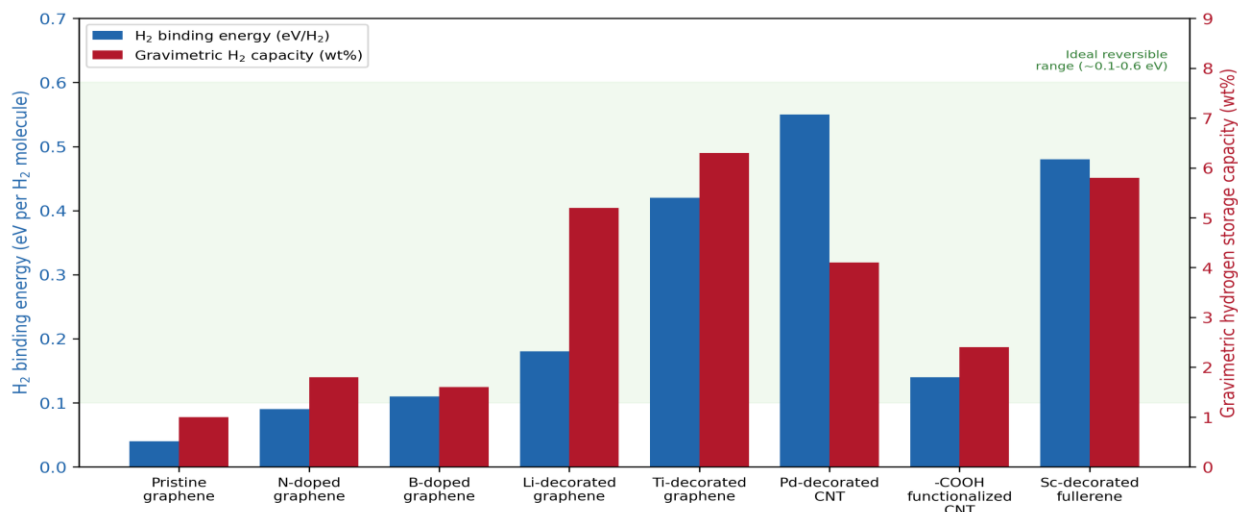


Figure 2: Comparative H₂ binding energies and gravimetric hydrogen storage capacities reported for representative functionalized carbon nanomaterials, synthesized from the first-principles studies

Table 2: Summary of H₂ binding energies, gravimetric capacities and adsorption mechanisms reported for representative functionalized carbon nanomaterials

Functionalized system	H ₂ binding energy (eV/H ₂)	Gravimetric capacity (wt%)	Adsorption mechanism
Pristine graphene	0.04	1.0	Physisorption (vdW)
N-doped graphene	0.09	1.8	Weak chemisorption at defect
B-doped graphene	0.11	1.6	Polarization-enhanced physisorption
Li-decorated graphene	0.18	5.2	Ion-induced electrostatic binding
Ti-decorated graphene	0.42	6.3	Kubas-type orbital interaction
Pd-decorated CNT	0.55	4.1	Dissociative chemisorption
-COOH functionalized CNT	0.14	2.4	Hydrogen-bond-assisted physisorption
Sc-decorated fullerene (C60)	0.48	5.8	Kubas-type / partial charge transfer

CHALLENGES AND COMPARISON WITH EXPERIMENTAL DATA

Metal-cluster agglomeration

One of the key issues in the first-principles literature is whether the calculated per-atom binding energies for isolated and uniformly-distributed metal atoms are representative of realistic materials that are synthesized in the experiment. Many transition and alkali metals have a thermodynamic driving force to cluster on a carbon surface (cohesive energy of the metal atoms is higher than the adsorption energy for the metal atoms on carbon) and ab initio molecular dynamics simulations of finite-temperature systems have demonstrated the ability of nominally well-dispersed decoration patterns to merge into larger clusters and/or nanoparticles under conditions relevant to device operation (Banerjee, P., Pathak, B., Ahuja, 2016). Cluster formation is usually not beneficial to storage performance because it decreases the number of catalytically and/or electronically active metal sites and may encourage bulk-like metal hydride formation that yields desorption temperatures that are significantly higher than those suggested by the single atom Kubas interaction. A number of the studies reviewed here explicitly address this issue, comparing the computed binding energy per metal atom with the cohesive energy of the corresponding bulk metal; doped substrates have often been found to provide superior binding of metal atoms compared to pristine carbon, and are therefore a necessary (although not sufficient) screen for identifying strategies for decoration that are likely to be stable against clustering.

Functional-dependent uncertainty in predicted binding energies

The accuracy of computed hydrogen binding energies depends on the way in which dispersion interactions are treated, and this is not just a technical point, but one which will lead to a variety of substantive disagreements in the literature on the size and even the sign of the predicted trends in hydrogen binding. The binding-energy variations have been reported as a factor of two or more when applying multiple dispersion-correction schemes (D2, D3, vdW-DF, vdW-DF2) to the same nominal system, with significantly smaller differences for the more strongly bound, orbital-mediated Kubas-type interactions, for which the dispersion contribution is a smaller percentage of the binding energy. This methodological uncertainty is most important right in the middle of the binding energy range where the reversible storage is most practically important, and it cautions against an over-interpretation of differences in quantitative measurements obtained in different studies using different dispersion treatments (Mousavi-Khoshdel, S. M., & Targholi, 2015).

Discrepancies between computational predictions and experimental measurements

A few of the functionalized systems described in Section 4 are included in the comparison of representative DFT-predicted gravimetric capacities with the experimentally reported values shown in Table 3. The experimental capacities in both examples are significantly lower than the computed capacities. This discrepancy is likely due to a variety of factors. Firstly, the decoration density of metals is not uniformly distributed in real materials, as assumed in periodic slab or a single cluster DFT models, that is, real materials do not have an ideal state of decoration and may have agglomeration and incomplete decoration, which diminishes the number of active binding sites. Second, the DFT binding-energy calculations are generally used for configurations with only one or a few molecules per unit volume of adsorbent, but the capacity measurements are always done with a fully loaded material, where the H₂-H₂ steric interactions and pore-filling effects can lower the achievable coverage from the single-site value (Gao, Y., Chen, M., Liu, 2022). Third, experimental measurements can be complicated by characterization uncertainties that arise from the need to accurately assess the accessible surface area, and the presence of physisorbed water or other adsorbates which may be present that compete for binding sites. This computational-experimental separation is one of the most relevant unanswered problems in the field, and highlights the importance of studies of finite-temperature and finite-loading configurations, as opposed to the idealized single-adsorbate limits.

Table 3: Comparison of DFT-predicted and experimentally reported gravimetric hydrogen storage capacities for selected functionalized carbon nanomaterials

Material system	DFT-predicted capacity (wt%)	Experimentally reported capacity (wt%)
Li-decorated graphene	5.2	1.2–1.8 (ambient, agglomeration-limited)
Pd-decorated CNT	4.1	2.1–2.9 (77 K, 3 MPa)
N-doped porous carbon	1.8	1.5–2.0 (77 K, 1 bar)
–COOH functionalized CNT	2.4	1.1–1.6 (room temperature)

FUTURE RESEARCH DIRECTIONS

Many pathways seem to be pointing in the same direction for the future of « first-principles » studies of interactions between hydrogen and carbon nanomaterials.

1. The number of possible combinations of various dopant elements, functional groups, decoration densities and co-functionalization patterns is much larger than can be explored exhaustively using traditional DFT, and can be explored by the use of high-throughput and machine-learning accelerated screening. A path toward screening thousands of candidate functionalized structures at a computational cost several orders of magnitude less than direct DFT is provided by machine-learned interatomic potentials trained on DFT reference data, and graph-neural-network models trained to predict the adsorption energy directly from structural descriptors, with the most promising structures then checked at full DFT accuracy.
2. Possible need for first principles modelling, going beyond the single-adsorbate, zero-temperature binding-energy calculation, to ab initio or machine-learning-potential molecular dynamics calculations of fully loaded, finite-temperature systems, which can capture agglomeration, H₂-H₂ crowding and entropic contributions to the free energy of adsorption not accessible to static 0 K calculations.
3. We see that the uncertainty regarding the choice of functional used and the lack of information regarding the benchmarks, which are linked in Section 5.2, could be clarified by further application of these higher accuracy methods (non-local van der Waals functionals, random-phase-approximation and quantum Monte Carlo

benchmarks) to larger functionalized systems, and the higher accuracy methods would give a stronger foundation for ranking of candidate materials calculated at the more affordable GGA-D3 level.

4. Systematic first principles studies of co-doped, co-functionalized architectures (e.g., nitrogen doped graphene decorated with titanium, or boron doped nanotubes functionalized with carboxyl anchored metal clusters) are likely to be more fruitful than ongoing studies of single strategy functionalizations of graphene and nanotubes.
5. The application of first-principles predictions to the real world depends on integration into device-scale and techno-economic models, to which the current literature is relatively limited and which is therefore a natural direction for interdisciplinary exchange and collaboration between computational materials scientists and chemical/mechanical engineers.

CONCLUSION

First-principles studies have been an important approach to defining the potential and the shortcomings of the functionalized carbon nanomaterials as hydrogen storage. Heteroatom doping, covalent oxygen functionalization and, most effectively, metal decoration can be used to increase the hydrogen binding energy from the physisorbed value, which is negligible in the case of pristine carbon, and bring it into, or into the vicinity of the thermodynamically favorable window for reversible storage at ambient temperature, as is convincingly demonstrated by the calculations based on DFT. The metal decoration by a Kubas-type orbital interaction emerges as the most consistently effective single method across the considered studies. Concurrently, there are significant challenges that have been identified, but not addressed in this review, such as the habit of metal atoms of clustering under realistic conditions, the disparity between computed and experimental binding energy values (which remain non-trivial), and the tendency for a particular dispersion-correction scheme to affect the computed binding energy. To overcome these challenges, first-principles simulations of the complex materials that are synthesized in the laboratory will need to go beyond idealized, single-adsorbate, zero-temperature calculations to finite-temperature, finite-loading and machine-learning-accelerated simulations. In conclusion, first-principles guided design of functionalized carbon nanomaterials is a promising, though not actually realized pathway, to the design of practical hydrogen storage materials for solid-state storage.

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